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A STUDY OF THE EXCHANGE CHARACTERISTICS OF MONTMORILLONITE CLAY FOR FISSION PRODUCT CATIONS FOR USE IN THE GENERATION OF INSOLUBLE AEROSOLS

by

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ABSTRACT

The exchange of cesium, cerium, strontium and yttrium with exchangeable ions in montmorillonite clay in aqueous suspension has been studied. The percent of the initial ion concentration exchanged into the clay has been determined as a function of the initial concentration. This data is useful in the preparation of clay having a high specific activity. It was found that clay can be prepared which has a specific activity of 2 mCi per mg for ^{137}Cs and 6 mCi per mg for ^{91}Y and ^{144}Ce.

(NOTE: In this report reference to quantities of the parent ^{137}Cs or the parent ^{144}Ce implies equilibrium quantities of the daughter ^{137}Ba or the daughter ^{144}Pr, respectively.)

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A STUDY OF THE EXCHANGE CHARACTERISTICS
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INTRODUCTION

Natural occurring clays are being used in waste disposal of radio-active products. This method utilizes the cation exchange properties of the clays. Ginnell and Simon[1] also made fused, tagged clay microspheres and suggested the use of the spheres for tracer studies and radiotherapy. This information led to the investigation of montmorillonite clay for use as a common vector for both single and mixed fission product insoluble aerosols. The work was initiated by Posner and Bennick[2] and continued as reported here to study the exchange of several individual isotopes into clay.

The clay aerosol is produced from a fine clay suspension by aerosol-izing the suspension and passing the tagged raw clay through a heat column maintained at 1100°C. Spherical clay particles are formed that are used in animal inhalation exposures. The aerosol particles made in this way are quite insoluble in the animal[3]. Amphlett[4] and Ginnell and Simon[1] report that when the clay is fused or just heated to a temperature greater than 500°C water is lost irreversibly from the lattice and the exchanged cations become a part of the lattice itself, where they are firmly held against further exchange.

CLAY EXCHANGER PROPERTIES

Many ion exchange experiments have been carried out with natural occurring alumino-silicate clays[1, 5, 6, 7, 8, 9]. The network structure of montmorillonite clay is composed of alternating layers of silicate tetra-

hedra and aluminate octrahedra. The ideal basic formula for montmoril-
lonite clay is $Si_8Al_4O_{20}(OH)_4 \cdot nH_2O$. The framework of the clay acquires
a net negative charge when ions such as Mg(II) and Fe(II) replace Al(III),
or Al(III) replaces Si(IV) in the clay network. This negative charge is
compensated for by cations which move freely between the layers of the
framework.

Ion exchange reactions between insoluble ion exchangers suspended
in solution and ions in solution are usually reversible reactions. In a
simple, workable model these reactions can be represented for cation ex-
changes by the general formula

$$\overline{mA}^{+n} + nB^{+m} \rightleftharpoons mA^{+n} + \overline{nB}^{+m}, \tag{1}$$
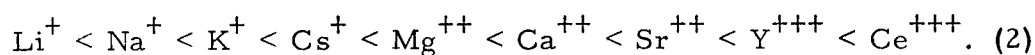
where A and B represent exchangeable cations and quantities with bars
refer to the inside of the clay exchanger. The common anions of the solute
play little part in the exchange. The law of mass action appears to hold
and in time ion exchange equilibrium is attained. However, the concen-
tration ratios of the two ion species are not necessarily the same in both
the exchanger and the solution phase. Factors which increase the selec-
tivity of the exchanger for a given cation include higher valence and smaller
solvated volume. It seems evident that in order to completely pack the
clay exchanger with a given cation, an excess of the cation is needed in
the supporting solution, but an excess of any ion of low charge and large
solvation size in the solution phase will replace any cation from the ex-
changer.

Sorption of an electrolytic solution by the clay takes place as well as
exchange. This perhaps is more important in a two-dimensional layered
clay, such as montmorillonite, than in three-dimensional lattice exchang-
ers. According to Helfferich[10] montmorillonites swell anisotropically
and appear to have several different stable interlayer distances depending
upon the degree of solvation of the exchanged ions. Sorption is usually
reversible and the cations can be removed from the exchanger by washing
with pure solvent.

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The exchange capacity of Bayard, New Mexico montmorillonite clay has been reported to be from 1.17 to 1.36 meq per gram of clay at room temperature[4,7]. Eliason[7] reported the formula $(Al_{3.14} Fe_{.152} Mg_{.60})$ $(Si_8) O_{20}(OH)_4 (Na_{.18} Ca_{.21})$ for this clay, in which the first parenthesis represents octahedrally coordinated ions, the second, tetrahedrally coordinated ions and the last exchangeable cations. The calculated exchange capacity is about one meq per gm of clay. Exchange in montmorillonite clay takes place by the entry of the ion into the inter-layer spaces. The particle size of the clay in suspension has little effect upon the exchange capacity of montmorillonite[4].

Gaines and Thomas[11] established a method to calculate an equilibrium constant for the reaction represented in Eq. (1). The Gibbs free energy is calculated from the constant. For the ion exchange reactions involving most cations, the free energy of reaction is less than ten kcal per mole. This is two or more orders of magnitude less than the free energy of reactions such as the oxidation of metals or the burning of organic fuels.

From the thermodynamic data of several researchers[4,7,8,9], one observes that the selectivity sequence of montmorillonite clay for various cations is

$$Li^+ < Na^+ < K^+ < Cs^+ < Mg^{++} < Ca^{++} < Sr^{++} < Y^{+++} < Ce^{+++}. \quad (2)$$

EXPERIMENTAL PROCEDURES

The clay used in this work was prepared by first treating the raw clay with an excess of 30% hydrogen peroxide. This removes the organic material and breaks some of the clay into small particles. The clay particles that remain in suspension after the peroxide treatment are removed and cleaned by dialysis, the sludge is discarded. The projected area size distribution of the raw clay in suspension is approximately log-normal. The count median diameter of the clay prepared in this way is about 0.2 μ with a geometric standard deviation of about 1.8. The density of the suspended clay particles is 2.2 grams per cm^3. The weight density of the suspension was determined by weighing the clay remaining after evaporation of a given volume of the suspension at 80-90°C.

Since the natural form of the clay probably contains calcium or magnesium in the exchangeable cation positions, some clay was packed with sodium ion (Na-clay) to increase the selectivity of the clay for the chosen cation. The sodium packing was accomplished by adding a 5% NaCl solution to the clay suspension, decanting the supernatant from the flocculated clay, and repeating the process once. The clay was washed with deionized water until it no longer flocculated. The excess sodium ions were removed by dialyzing the suspension for about one week.

Since it would be desirable to predict the specific activity of the clay for any isotope, it is necessary to know the percent exchange as a function of the concentration of the exchanging cation. It is also desirable that the percent exchange be as high as possible, consequently the concentration of all other cations is kept as low as possible. To find the percent exchange as a function of cation concentration, tracer-level experiments were done with cesium, strontium, cerium and yttrium ions. The radioactive ions used were $^{137}Cs^{+}$, $^{144}Ce^{+++}$, $^{85}Sr^{++}$, and $^{91}Y^{+++}$. The chloride salt was used in each case. For all the tracer-level exchanges, except those of ^{91}Y, the activity of each radionuclide used in an exchange and the clay sample after the exchange was determined by photopeak analysis. The ^{91}Y stock solution was assayed using a β counter and carefully measured volumes of the solution were used in the exchanges; ^{91}Y-tagged clay was also β counted. In addition to these tracer-level exchange studies high-level exchange studies were done with $^{144}CeCl_3$, $^{91}YCl_3$ and $^{137}CsCl$ in order to estimate the maximum attainable specific activity for the clay.

Factors that could be varied in these tracer-level exchanges include stable ion concentration, pH, clay type and time. Most of these factors were varied with only one or two ions and the results of those experiments were judiciously applied to the other cations. Both cesium and strontium exchanges were done with natural and Na-clay. The plus three ions, cerium, and yttrium, were exchanged only into natural clay because of the high selectivity of the clay for these ions. All exchanges were done in neutral solution if chemically possible. The effect of the hydrogen ion concentration on cerium exchange was studied. All yttrium exchanges

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were done in 1N HCl solution.   It was found that in three hours as much cesium is exchanged into the clay as overnight (16-20 hrs.) This agrees with the work reported by Sawhney[12]. However, since it was more convenient, overnight exchanges were done.

The batch exchange technique was used in this work since it has been planned to use such a technique when preparing the clay for animal inhalation exposures.   The procedure was to pipette approximately 0.5 ml of the tracer level (1-5 µc) radioactive salt solution into a small polyethylene container, γ count the solution (except for ^{91}Y as mentioned earlier), add the stable salt, a known amount of clay (10-20 mg) and finally water or HCl to make a final volume of 3 ml with the desired pH.   The exchange was allowed to take place overnight; the container was shaken occasionally during the exchange. After the exchange, the suspension was vacuum filtered on a type HA or UG Millipore filter, the cup rinsed out with approximately 3 ml of deionized water and the vacuum filter stack rinsed with about 3 ml of water.   The filter was taped with cellophane and γ or β counted.   The filtrate was discarded.

The high-level exchanges were done in the same way except that all the activity levels were obtained by assaying small volumes of the solution. In the cerium and yttrium exchanges, about 5 mg of clay was added to about 1 ml of solution containing on the order of 50 mCi of the radionuclide. The cesium high level exchanges were done during the preparation of some radioactive clay microspheres for inhalation experiments.   In that work, 60 mCi of cesium was added to 24 mg of clay in a total volume of 3 ml.

RESULTS

The principal results of the tracer-level experiments are shown in Fig. 1.   The percent exchange of the cations from the solution into the clay is shown as a function of the combined cation concentration in the clay and the solution.   The conditions used during these exchanges were pH 6 and Na-clay for cesium and strontium, pH 6 and natural clay for cerium, and 1N HCl solution and natural clay for yttrium.   These conditions give the best fraction of exchange for each of the ions.   Figs. 2 and 3 illustrate that the percent exchange is higher for cesium and strontium into Na-clay than into natural clay.   The pH of the solution in the
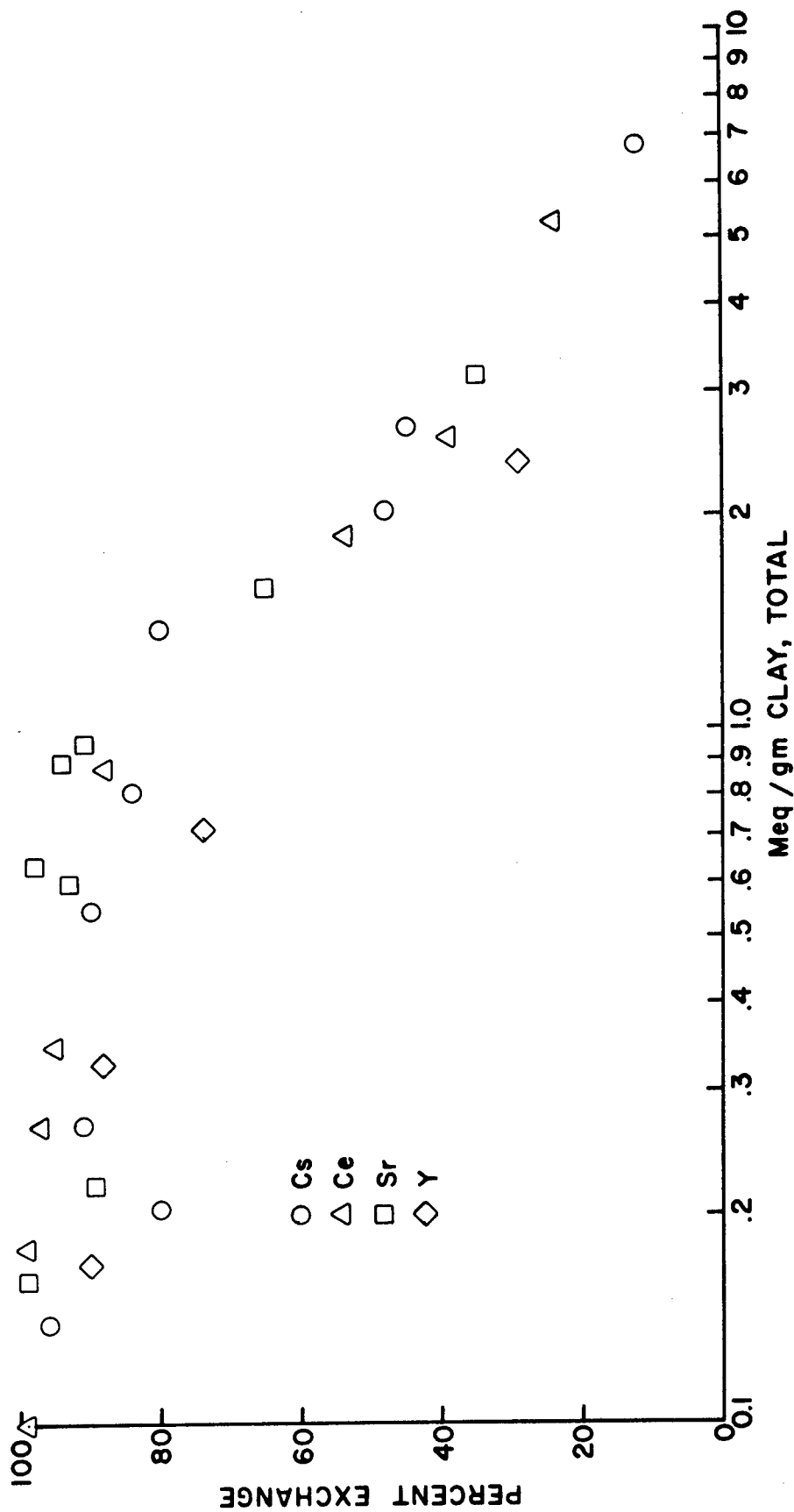
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Figure 1.   Percent exchange as a function of ion concentration.   Conditions were: natural clay and pH 6 for cerium, Na-clay and pH 6 for strontium and cesium, and natural clay and pH ~ 0 for yttrium.
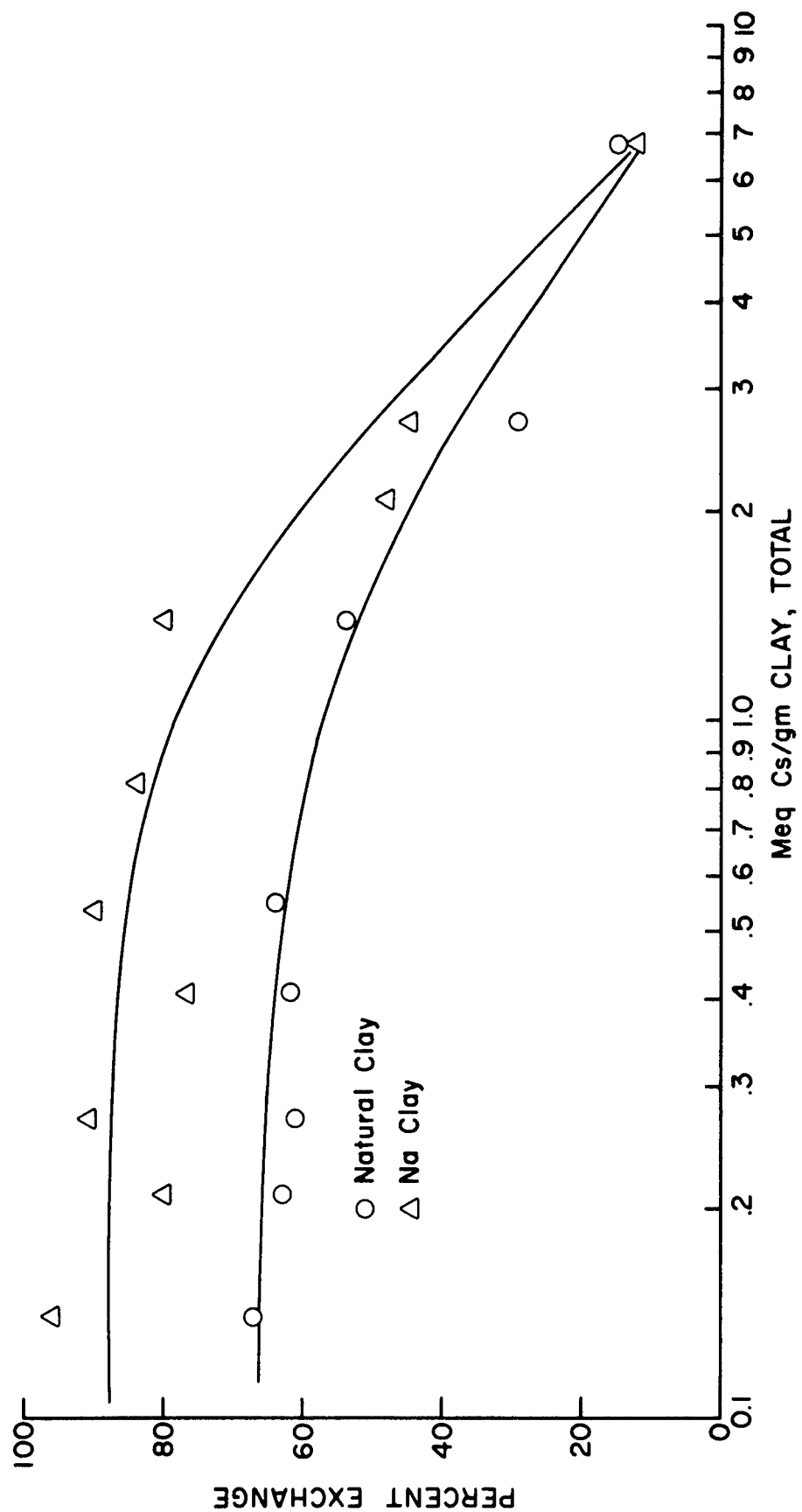
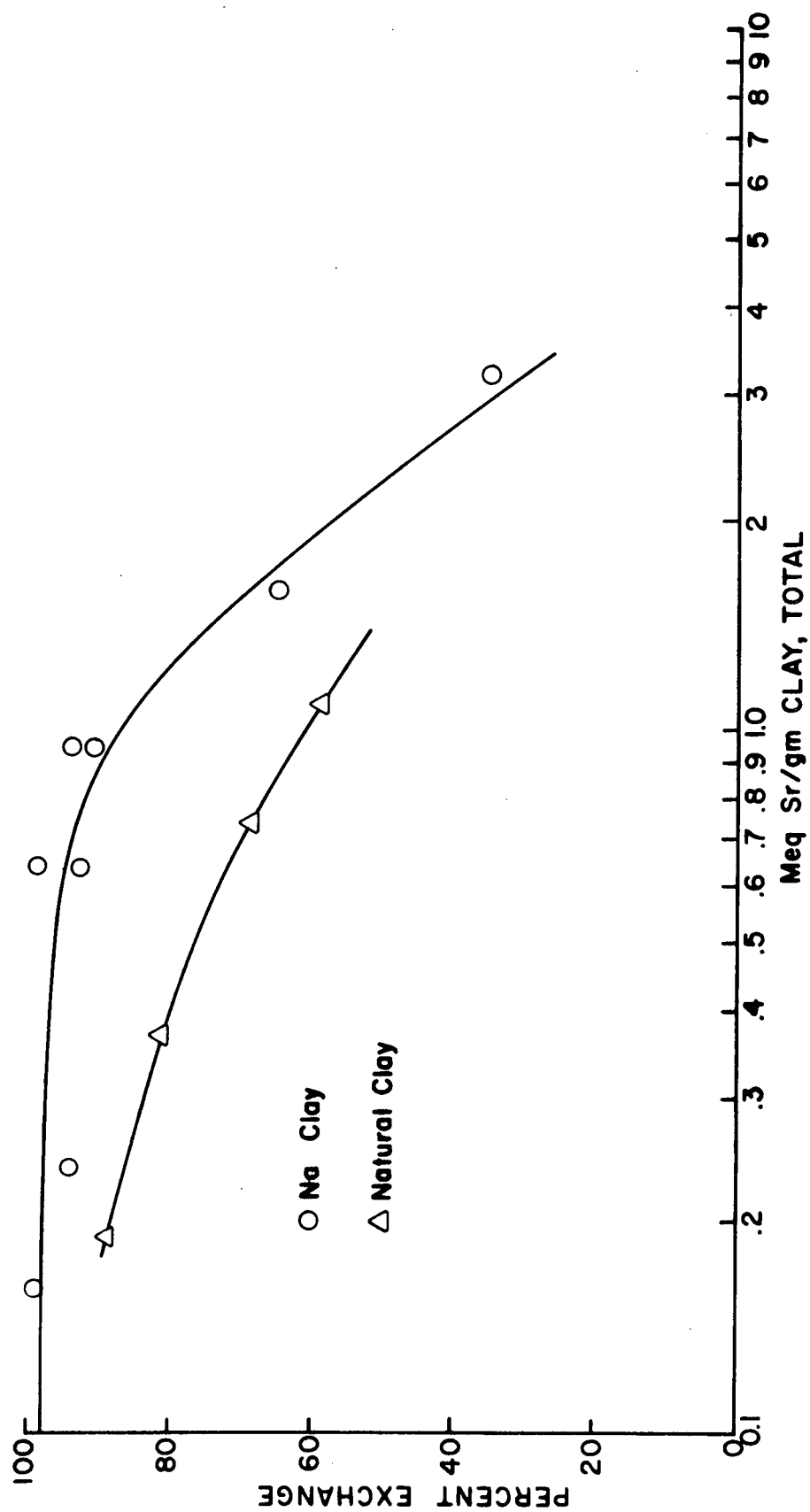Figure 2. Percent exchange as a function of cesium concentration

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Figure 3. Percent exchange as a function of strontium concentration

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range 1.2 - 6 did not significantly influence the exchange of cerium into clay as shown in Fig. 4. However, the percent of yttrium exchange in 1 N HCl solution appears to be lower than the others as illustrated in Fig. 1.

The data from the high-level exchanges including the initial concentrations of the solutions, the percentage exchange and the final specific activity of the clay are listed below.

Isotope	Initial mCi/mg clay	% exchange	Final mCi/mg clay
^{137}Cs	2.5	70	2
^{144}Ce	9.8	60	6
^{91}Y	16.0	40	6

Estimates of the specific activity of the nuclide in solution can be made from the percent exchange in the high-level exchanges and Fig. 2. For example, the 60% exchange of cerium reported above implies a concentration of about 1 meq per gram of clay or .05 mg of cerium per mg of clay and a specific activity of cerium of 120 mCi per mg. Contaminating ions in the radionuclide source material will reduce the apparent specific activity and the amount of the radionuclide that will exchange with the clay. When the specific activity of the nuclide is known, an estimate of the specific activity of the clay for an initial concentration ratio can be made. By increasing the initial ratio of ion to clay concentration a somewhat higher clay specific activity could be obtained.

SUMMARY

The exchange of cesium, cerium, yttrium and strontium into montmorillonite clay was investigated. The percentage exchange of the isotope is nearly the same for all four ions on a meq per gm of clay basis if the optimum conditions are used in the exchange. Knowing the specific activity of the nuclide as received, it is possible to predict the specific activity of the radioactive clay. The total exchange capacity of the clay being used appears to be about 1.2 meq per gm of clay. Of course, in order to reach the total capacity either an excess of the exchanging ion must be present in the solution, or the ions which are being exchanged out
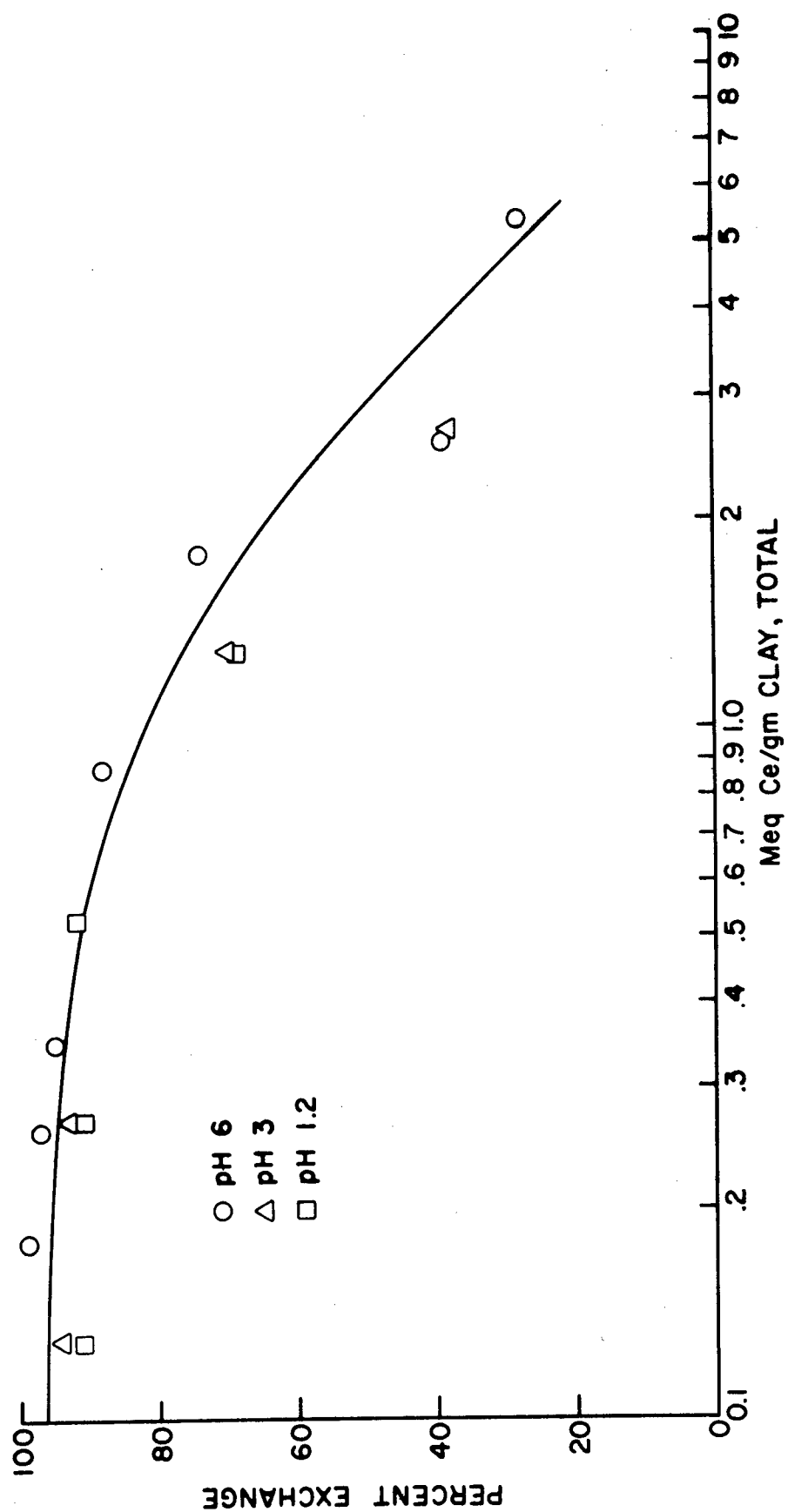
Figure 4. Percent exchange as a function of cerium concentration

of the clay must be removed from the solution.

Since the specific activity of the radionuclide as received in solution is usually not known, pilot exchanges would have to be done with the nuclide to determine the initial concentration ratio of ion to clay needed to obtain the desired clay specific activity. If enriched nuclides were available, very high clay specific activities would be attainable for nuclides having short half lives.

ACKNOWLEDGEMENTS

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